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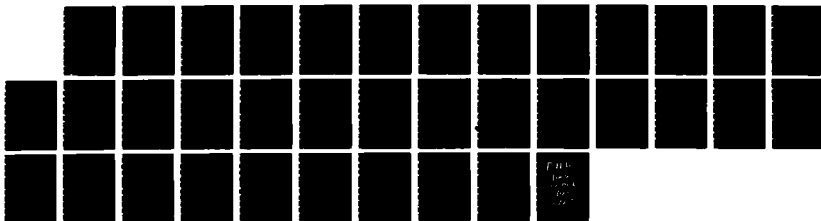
THERMOPLASTIC ELASTOMERS AS LOVA BINDERS(U)
MASSACHUSETTS UNIV AMHERST DEPT OF POLYMER SCIENCE AND
ENGINEERING J C CHIEN ET AL 1987 N00014-85-K-0880

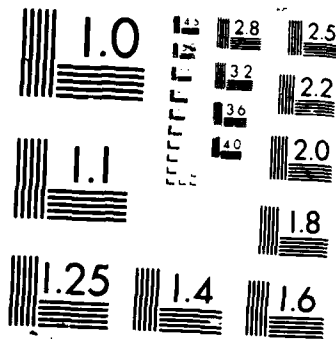
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Quarterly Report

Project: Thermoplastic Elastomers as LOVA Binders

Contract No.: N00014-85-K-0880

Period of Report: April 1987 to July 1987

Principal Investigators: Professor James C.W. Chien
Professor Richard J. Farris
Professor C. Peter Lillya
Professor H.H. Winter

Postdoctoral Fellows: Y.G. Cheun
P.W. Jin
R. Zhou
F.A. Kim
Y.G. Lin

Ph.D. Candidates F.A. Morrison
D.T. Hseih
E. Kolb
L.L. Anderson
T. Stephens
K.F. Auyeung

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Publications

"Simulation of Welding Flows, Part 2 - Stress Calculations Compared with Experimental Data", K.H. Wei, M.E. Nordberg, III and H.H. Winter, accepted for publication in Polymer Engineering and Science, 1987.

"A Simple Equation for the Steady Shear Viscosity of Filled Polymer Melts", T.S. Stephens and H.H. Winter, in preparation, 1987.

"Structure-Property Relationships in Thermoplastic Elastomers IV. Dynamic Mechanical Relaxations in Poly(dioxolane), Poly(butyltrioxocant) and Poly(propylene oxide) Polyurethanes", J.C.W. Chien and M.K. Rho, J. Appl. Polym. Sci., submitted 1987.

"Liquid Crystalline Compounds and Polymers from Promesogens", J.C.W. Chien, R. Zhou and C.P. Lillya, Macromolecules, submitted 1987.

"Cationic Polymerizations of 2-Substituted Dioxepanes", C.P. Lillya, Y.G. Cheun and J.C.W. Chien, Macromolecules, submitted 1987.

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Technical Reports Issued

Number 20 "The Modelling of Orientation in Planar Polymer
Welding Flows"

Number 21 "Synthesis and Characterization of Block Copolymer"

Number 22 "Synthesis and Characterization of Block Copolymers"

I. Advanced Cry/am TPE

A. Synthesis of Crystalline Segment - poly D/T

Polytrioxane/dioxolane with different T_m ($T_m = 48.39, 73.19, 98.59$ and 139.16°C) have been synthesized by using toluene as the solvent (Fig. 1 - 4). The compositions of P D/T ($T_m = 48.79, 73.19$ and 98.59°C) were measured by ^1H NMR (CDCl_3): trioxene content increased from 0.41 to 0.65. The molecular weights of these poly D/T were determined by Karl-Fisher method (LAH in O) as 2000 ~ 25000. P D/T ($T_m = 139^\circ\text{C}$) is insoluble in common O solvent, therefore, its composition was determined by solid C NMR: T/D = 0.748/0.252.

Different solvents have been used instead of toluene. It was found that CHCl_3 is suitable for this reaction, the yield of P D/T ($T_m = 100^\circ\text{C}$) increases from 5% (toluene as solvent) to 35%.

B. Fractionation of poly D/T

Poly DT #32 from Olin Company was not homogeneous. Three sampling gave three different DSC traces with different area ratios of low melting to high melting components. A vareity of solvent have been tried to fractionate those two different melting ranges, and halogenated solvents are much better than common organic solvents. The soluble fraction from chloroform has two T_m peaks 85, 105°C . Fraction soluble in methylene chloride and dichloroethane showed one T_m at 85°C . Tetrachloroethane soluble materials showed rather wide range of melting behavior. Comparison of the soluble fractions from methylene chloride and dichloroethane at 50°C showed the former

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to possess higher melting fraction than that of the latter fraction. Comparison of the soluble fraction from dichloroethane at 50°C and 64°C showed the latter to be higher melting fraction than the former.

C. Pyrolysis of PDT

Methylene chloride soluble fraction showed that it was very stable. A very minor weight loss was observed around 270°C with significant weight loss beginning at 400°C. In the presence of ethyl naphthalene sulphonate as latent acid. A significant weight loss was observed around the decomposition temperature of ethyl naphthalene sulphonate. For the protonic acid as p-toluene sulfonic acid. The PDT started to decompose by 100°C.

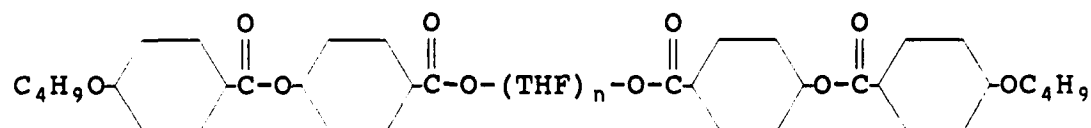
D. Synthesis of Cry/am TPE

PD/T and P4MeDOL were coupled by MDI to form polyurethane (PU). The product is a light yellow elastomer. This reaction can be monitored by IR. The intensity of isocyanate peak (2270 cm^{-1}) decreases and a new peak at 3300 cm^{-1} (N-H stretch) appears indicating the formation of urethane block. DSC results showed good phase separation behavior, the melting transitions of PU are the same as PD/T, even at very low hard segment (PD/T) composition 10 wt %. This result was also proved by polar microscopy. All the PUs thus made are acid sensitive, TGA results showed that PU started to decompose at 286°C and wt lost was 87% during 420 - 480°C. If toluene sulfonic acid (5 wt %) was added, it started to decompose at 99°C and wt lost was 78% during 99 - 178°C.

II. Advanced Liquid Crystalline TPE

A. Twin LC TPE

Liquid crystalline polymers have been synthesized with PTHF soft spacer for



Ia	n = 8.8	MW = 1232
Ib	n = 13.6	MW = 1592
Ic	n = 28	MW = 2592

The structure of the polymers were identified by IR of NMR-200.

The ^1H NMR results for the polymers are:

δ 1.00 ppm (CH_3), 1.61 (butyl H_γ), 1.84 (butyl H_β), 3.44 (THF CH_2), 4.06 (butyl H_α), 4.35 (CH_2 ester), 6.99 (3.5-oxybenzoate), 7.30 (3.5-oxybenzoate), 8.13 (2.6-oxybenzoate).

The molecular weight of the polymers can be calculated by integrated ratios.

Transition temperature of the polymers from DSC) are:

	T_m °C	T_i °C
I _a	28	50
I _b	25	60
I _c	24	55

The mesophase can be observed on polarizing microscope between T_m and T_i .

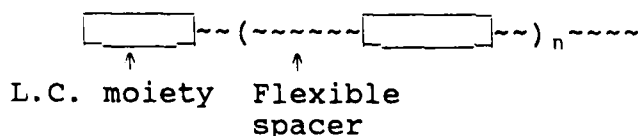
Thermodynamic parameters

	T_i ($^{\circ}\text{K}$)	MW	ΔH cal g^{-1}	ΔH cal M^{-1}	ΔH $\text{cal M}^{-1} \text{ K}^{-1}$	Mesogen Wt %
I_a	323	1232	0.34	419	1.3	50
I_b	333	1592	0.22	350	1.05	38
I_c	328	2592	0.05	130	0.40	23

B. Segmented LC TPE

(1) Objective

To prepare a series of polymers with liquid crystalline hard segments and long flexible spacers.



(2) Results and Discussion

In the previous report a series of polyesters were reported that contained two ring azo and azoxy benzene moieties. None of these polymers exhibited liquid crystalline behavior. The inability of these materials to form a mesophase could be due to inefficient phase separation. One way to overcome this would be to increase the length of the mesogen. Two methods are being explored to prepare these polymers. The first calls for the preparation of a functionally endcapped prepolymer. This material can then be polymerized with a number of aromatic dicarboxylic acid chlorides.

The second method enlists chain extension polymerization

techniques. Here short spacers, butanediol (BDO) for example, are used to link together the mesogenic units.

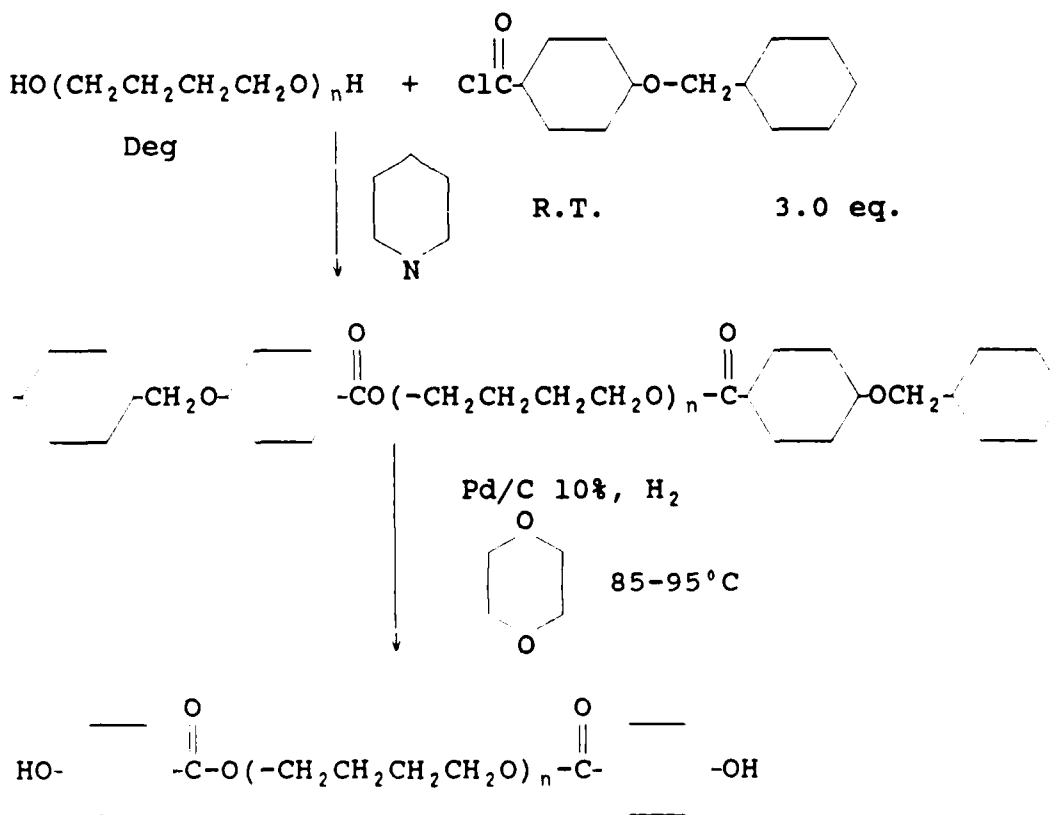
(3) Preparation of Endcapped Prepolymer

The endcapped functional prepolymer was prepared by reacting poly THF 650 with three equivalents of p-benzyloxy benzoylchloride in pyridine.

A number of debenzylations were investigated to reveal the functionalized material. Here only catalytic hydrogenation gave satisfactory results.

Reaction Scheme I

Preparation of functionalized endcapped prepolymer.



This endcapped material has been characterized by ^1H NMR, IR and thin layer chromatography and is greater than 95% pure. When the L. Kely impurities are monodebenzylated material.

This material will e polymerized with aromatic and aliphatic diacid chloride and investigated for liquid crystalline properties.

(4) Multiple Rings Joined by Short Spacers

Here two polymers have been prepared using azobenzoyl chloride as the hard segment, butane diol as the chain extender and poly THF as the soft segments. These results are in Table 1

Table 1

Polymer	Soft Segment	T.P.E.?	L.C.
1	Poly THF 650	No	?
2	Poly THF 2000	Yes	?

III. Cationic Copolymerization of 2-Butyl-1,3-Dioxepane with 1,3-Dioxolane

Copolymerization of 2-butyl-1,3-dioxepane (Bu-DOP) (A) with 1,3-dioxolane (DOL) (B) was studied with borontrifluoride etherate ($\text{BF}_3 \cdot \text{OCC}_2\text{H}_5$)₂) as initiators. It was followed by determining the unreacted monomers by means of gas-chromatography. The time-conversion curves in Fig. 1 and Fig. 2 showed that preferential polymerization of 2-butyl-1,3-dioxepane occurred. In the case of the copolymerization of 2-butyl-1,3-

dioxepane and increased, the polymerization of dioxolane gradually slowed down. At this stage the concentration of unreacted Bu-DOP and DOL monomers were 2.8 ~ 3.0 and 4.0 ~ 4.3 mol/l, which is considerably higher than the equilibrium monomers concentration of Bu-DOP and DOL were 1.87 and 1.56 mole/l at -10°C. The ^1H -NMR spectrum of one of the copolymer shown in Fig. 3 presents six resonance signals centered at 0.87, 1.29, 1.60, 3.39, 3.56 and 4.42 ppm from TMS, which the composition of the copolymers were obtained from the intensities of the resonance at 3.39, 3.56 and 4.42 ppm. The results are listed in Table 1. A set of copolymerization with varying monomer compositions were made at lower conversion. The experimental results given in Table 1 were used to obtain the composition diagram shown in Fig. 4. The values of the reactivity ratios calculated by the Fineman-Ross were $r_A = 2.13 \pm 0.05$ and $r_B = 0.09 \pm 0.05$ at -10°C.

The isolated copolymers were measured DSC analysis with varying monomer compositions in Fig. 5. The T_g should vary with composition as shown in an expression by Fox equation, which the values (T_g) were agreed of these calculated and experimental quantities.

The higher reactivity of 2-butyl-1,3-dioxepane as compared with dioxolane agree with the higher basicity and propagating species.

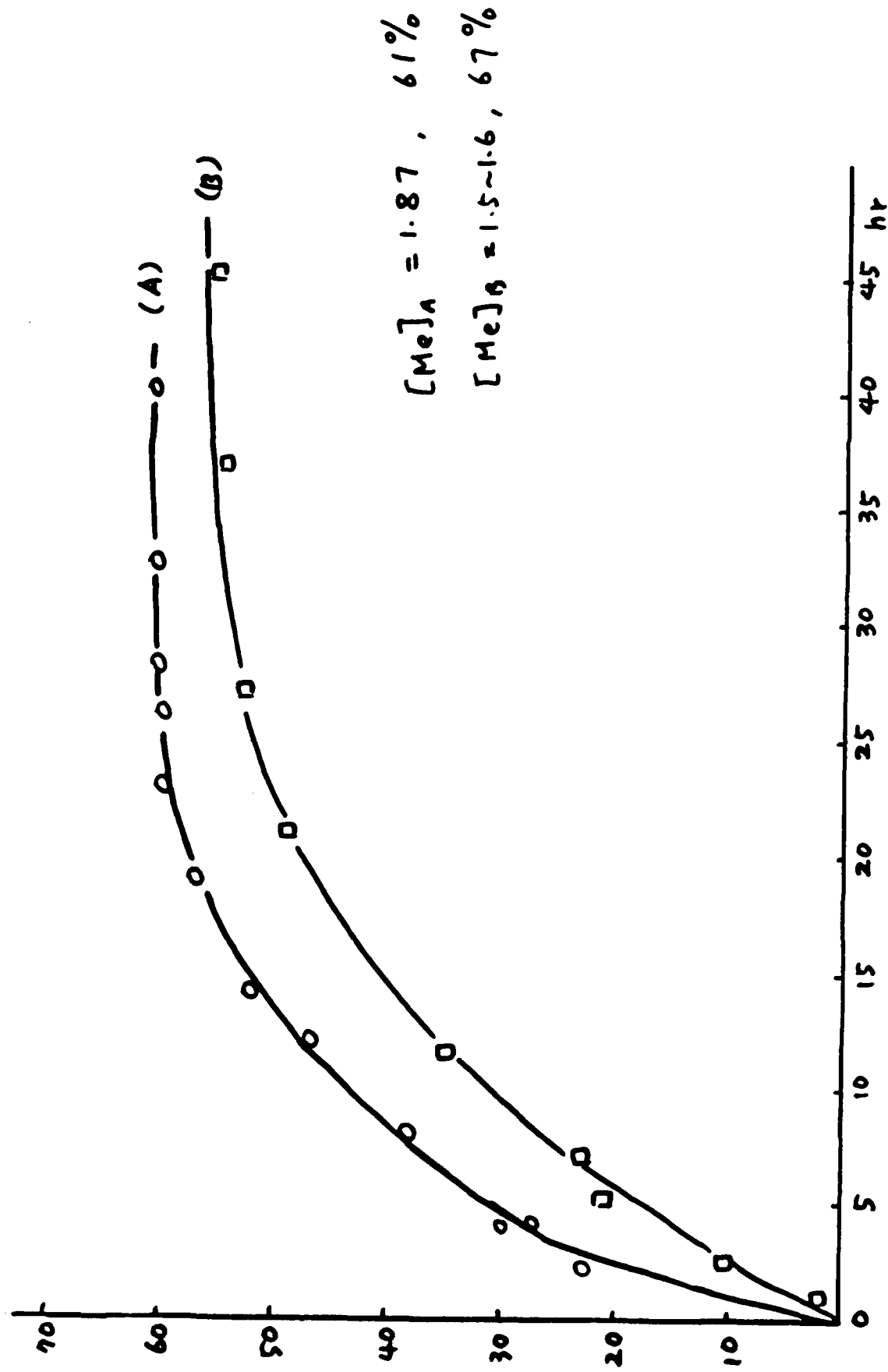


Fig. 1. Homopolymerization (A) of 2-butyl-1,3-dioxepane (Bu-DOP) and (B) of dioxolane (DOL) with $BF_3 \cdot O(C_2H_5)_2$ at $-10^\circ C$.
 $[Bu-DOP] = 4.8 \text{ mole/l}$; $[DOL] = 4.9 \text{ mole/l}$; $[BF_3 \cdot O(C_2H_5)_2] = 3.1 \times 10^{-2} \text{ mole/l}$.

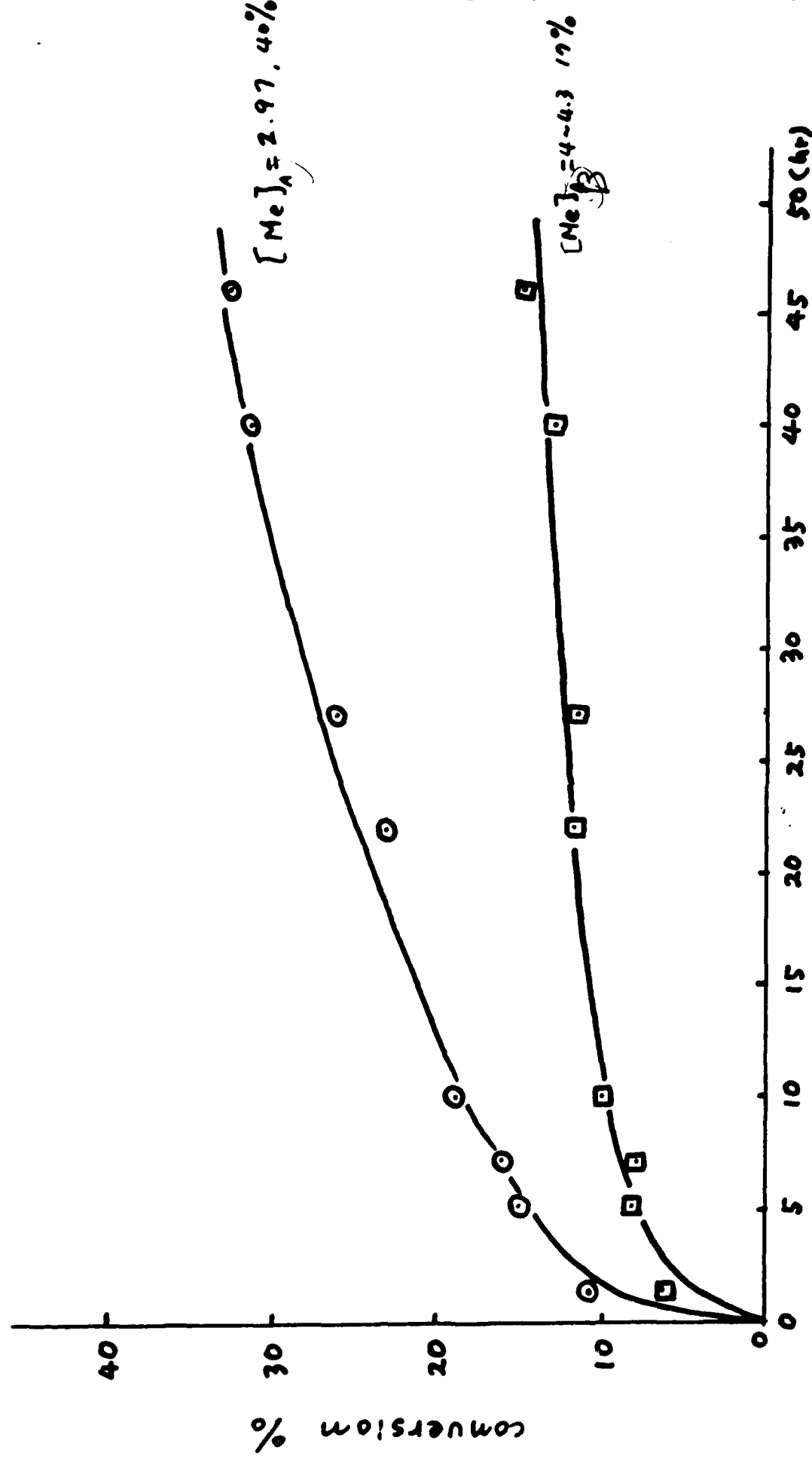


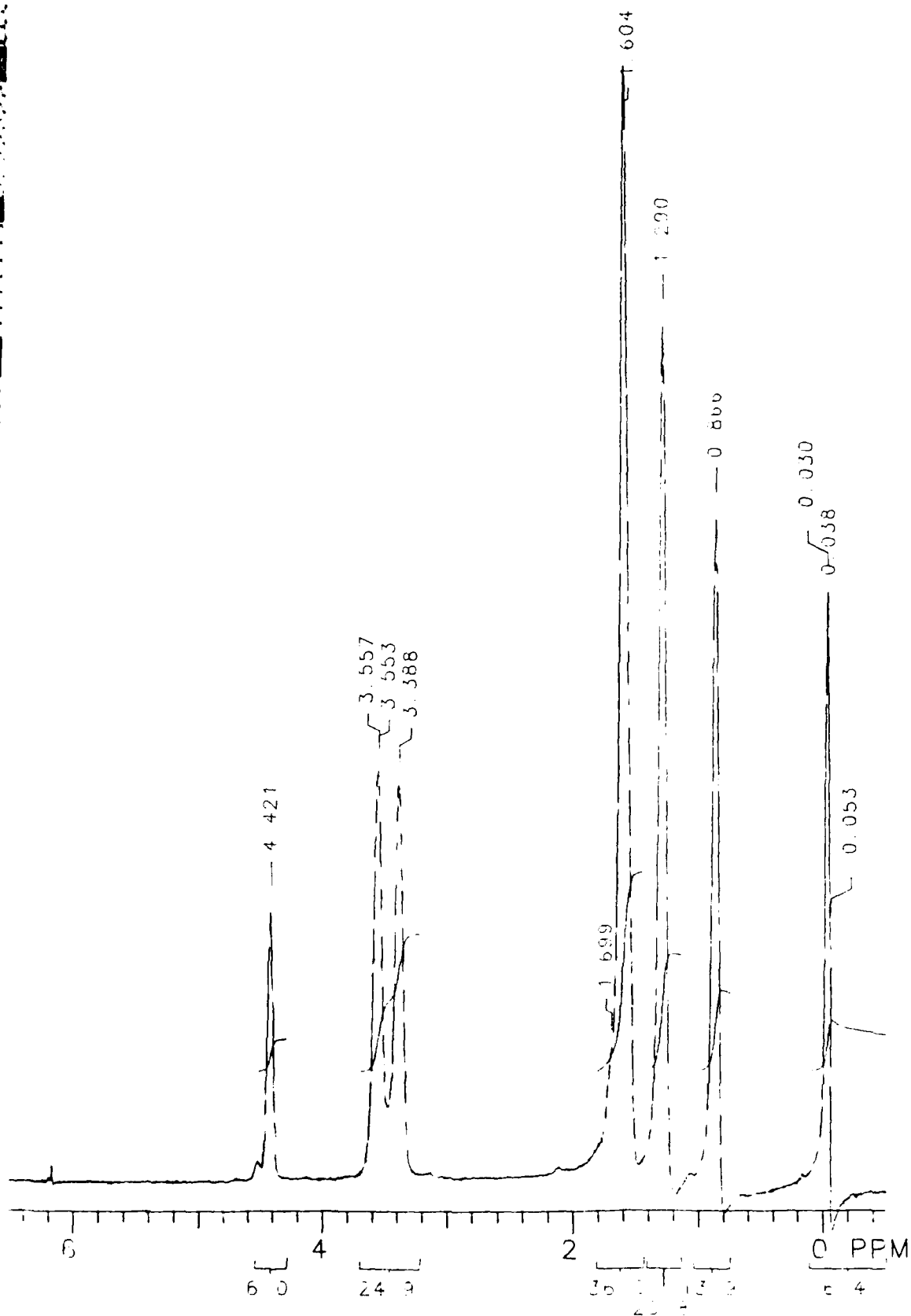
Fig. 2. Time - conversion curves for the copolymerization

of 2-butyl-1,3-dioxepane (○) with 1,3-dioxolane (◻).

$[Bu-Dop]_0 = 4.96 \text{ mole/l}$; $[DOL]_0 = 5.13 \text{ mole/l}$;

$BF_3 \cdot O(C_2H_5)_2 = 1.09 \times 10^{-2} \text{ mole/l}$; solvent: CH_2Cl_2 ; temperature $-10^\circ C$.

$$p(\text{Del } 1/3, \text{ Dop}) = 0.25$$



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XL300 PROTON
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SOLVENT CDCL3
FILE H

ACQUISITION		
IN	1.750	ON
SW	400.0	ON
AT	3.752	ON
NP	300.16	ON
PW	7.0	ON
P1	0.0	ON
D1	0.0	ON
D2	0.0	ON
TO	7.00	ON
NT	1.0	ON
CT	1.0	ON
PW90	9.0	ON
BE	0.0	ON
SS	0.0	ON
DE	0.0	ON
IN	0.0	ON
OP	0.0	ON
AS	0.0	ON

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Fig. 3

Table Copolymerization of 2-butyl-1,3-dioxepane (Bu-Dop)
and dioxolane (DOL) Catalyst: $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$, solvent:
 $(\text{CH}_2\text{Cl})_2$; temp. -10°C .

Monomer (mole/l)		$\frac{\text{DOL}}{\text{Bu-Dop}}$	DOL mole fraction	reaction time (hr)	conversion %	DOL in copolymer mole fraction
DOL	Bu-Dop					
5.76	1.28	4.5	0.82	30	5	.46
3.53	0.85	4.2	0.81	24	4	.40
5.42	2.04	2.7	0.73	15	8	.35
3.79	1.90	2.0	0.67	5	8	.31
2.83	2.54	1.1	0.53	3	9	.25
1.36	2.54	0.54	0.35	3	5	.15
0.74	2.54	0.29	0.22	12	7	.11

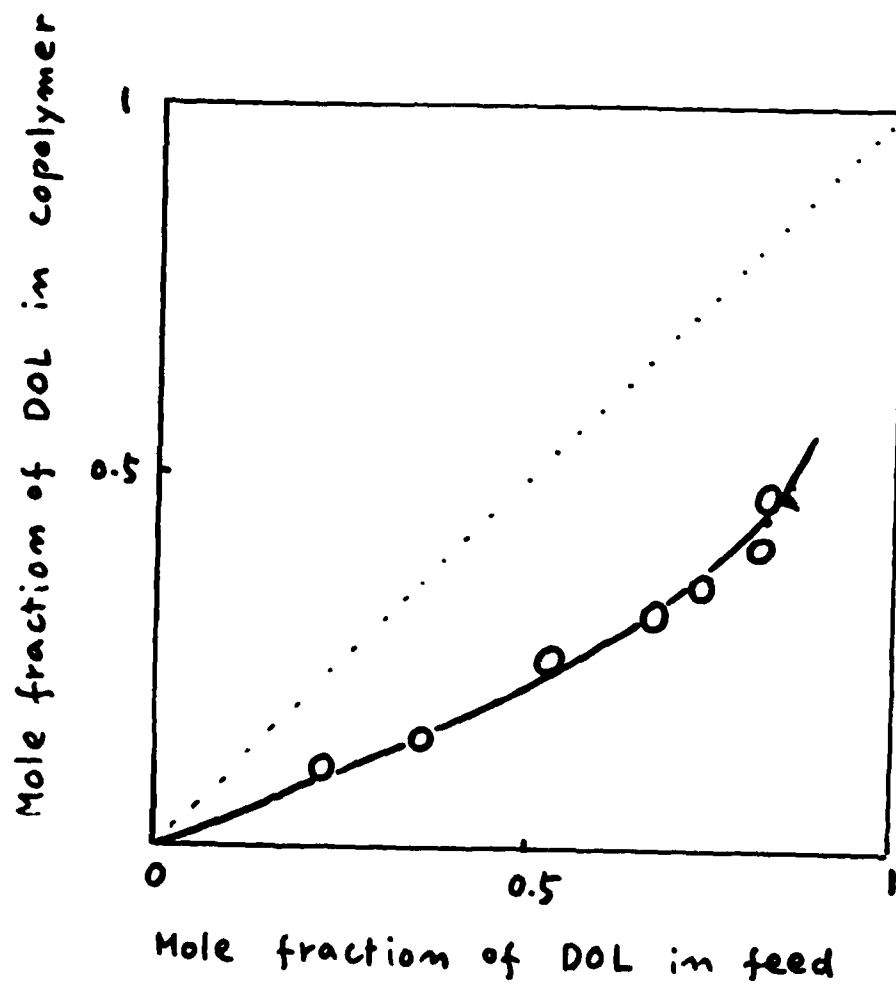


Fig.4. Copolymer composition curve of 2-Bu-Dop and DOL at -10°C .

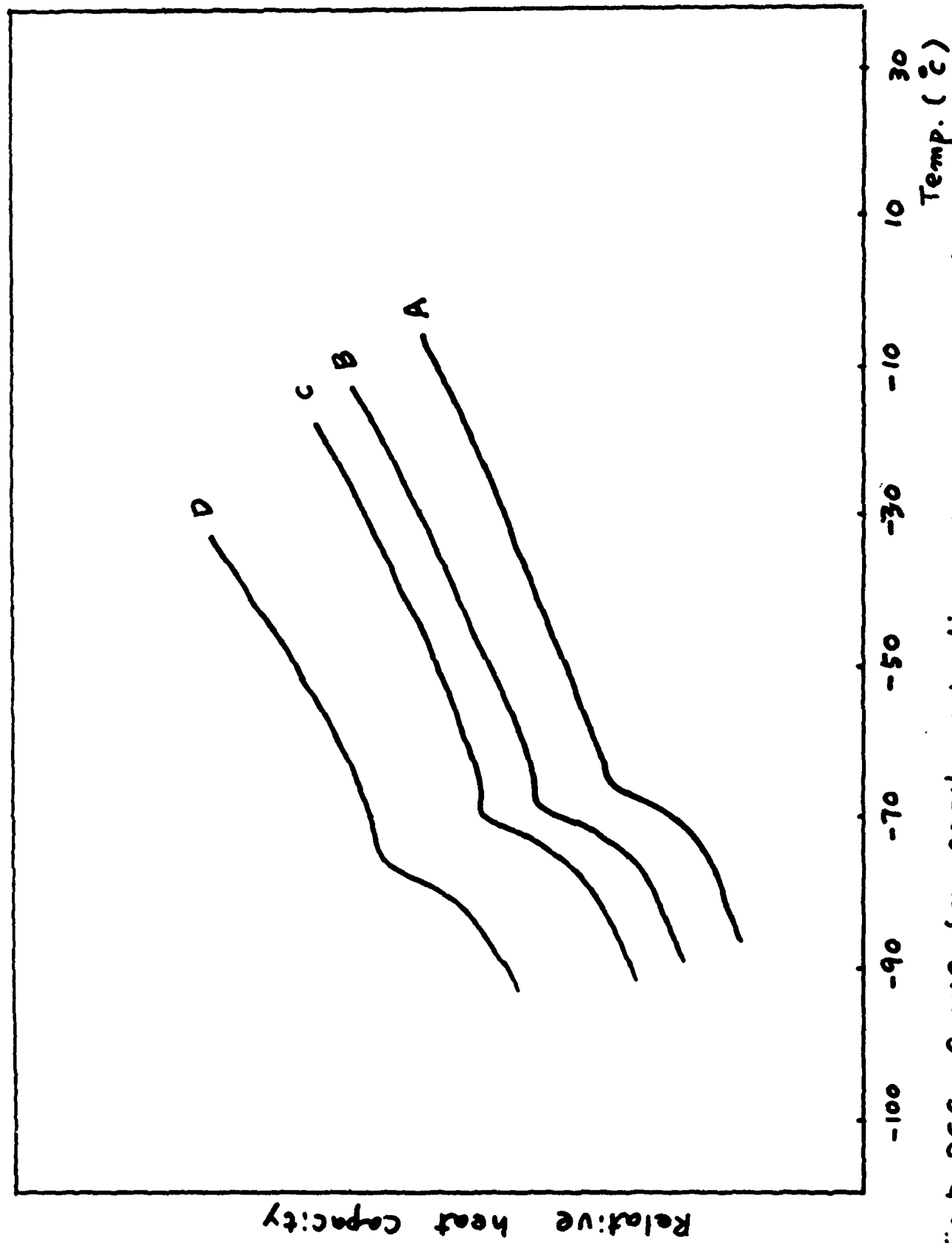


Fig.5. DSC Curve for copolymerization of 2-butyl-1,3-dioxepane with 1,3-dioxolane. A, Bu-DOP; B, 85:15 Bu-DOP/DOL; C, 75:25 Bu-DOP/DOL; D, 40:60 Bu-DOP/dioxolane.

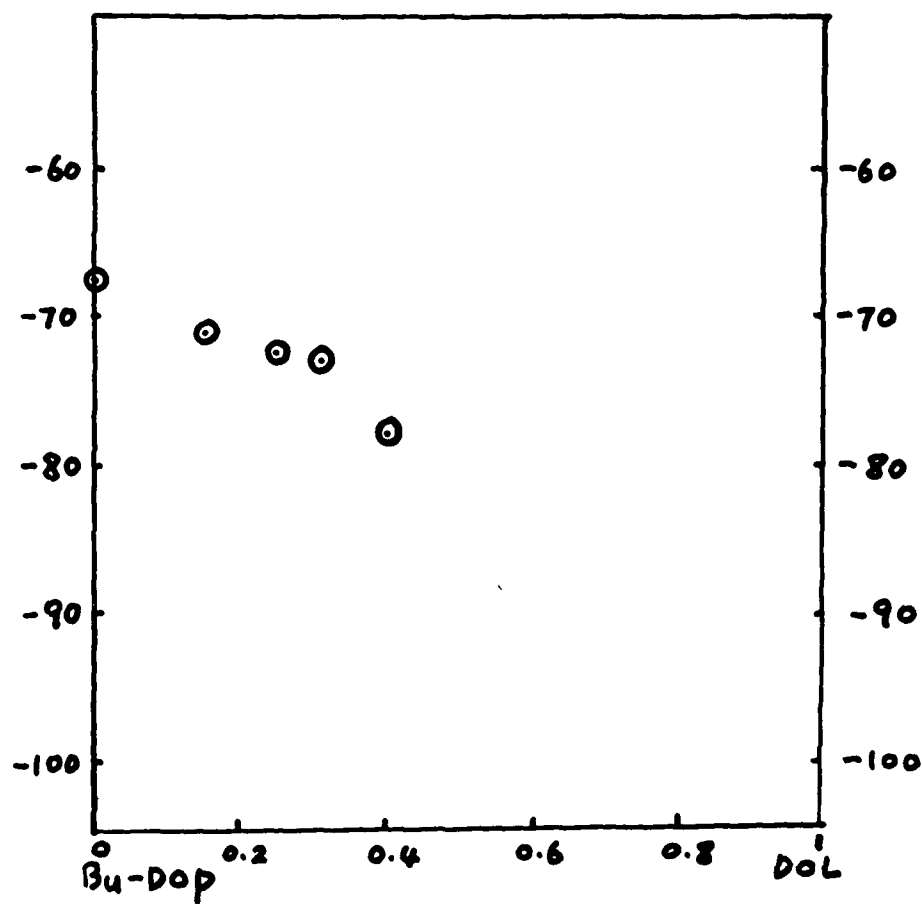


Fig. 6. T_g measured by DSC versus composition for copolymer (DoL/Bu-Dop)

IV. The Effect of Concentration of Components

A. The General Case

It has been shown that the observed concentration dependence of the apparent viscosity of a blend of linear and branched polymers can be described by the non-hydrodynamic and hydrodynamic contributions to the observed viscosity resulting from the redefinition in behavior of the polymer molecules in the blend. Equations based on the linear superposition of the two effects can be proposed to determine the viscosity of filled polymer blends as a function of filler concentration and filler volume fraction.

It is assumed that the observed viscosity curve for a filled polymeric liquid is similar to that for the polymer, that the observed shape of the viscosity-concentration curve can be described by linear superposition of the components, one for concentration and one for filler.

$$\eta_a = \eta_p + \eta_f \quad (1)$$

where each component has a concentration value of zero, zero rate and exponent, where the concentration at zero is zero. Inclusion in this equation of the concentration of the filler leads to the non-hydrodynamic and hydrodynamic contributions to the viscosity.

The observed behavior of the viscosity can be expressed by the generalization of the equation for a Newtonian liquid to give:

$$\eta_{ij} = \eta_{ij}^0 + \eta_{ij}^1 \dot{\gamma} + \eta_{ij}^2 \dot{\gamma}^2 + \dots$$

$$\eta_{ij}^0 = \eta_{ij}^0(\dot{\gamma}) = \eta_{ij}^0(\dot{\gamma}_0) + \eta_{ij}^1(\dot{\gamma}_0) \dot{\gamma} + \eta_{ij}^2(\dot{\gamma}_0) \dot{\gamma}^2 + \dots$$

The proposed equation can describe a wide range of shapes of the viscosity curves, and a hierarchy of parameters is introduced to describe the general case. Most of the parameters in the equation are determined by the properties of the unfilled liquid and the nature of the solid particles (dissipation considerations). The yield stress σ_y is a function dependent on the particle volume fraction, and on other properties of the particles which determine the non-hydrodynamic contribution to the interaction. The zero stress is introduced to describe the shear rate dependence of the parameters. However, the parameter η_{ij}^0 will be assumed to depend in some simple way on the rheological properties of the polymer itself, and the volume fraction of the fillers.

After substituting eq. (1) the equation takes the form

$$\sigma = \sigma_y + \eta_0 \dot{\gamma} + \eta_1 \dot{\gamma}^2 + \eta_2 \dot{\gamma}^3 + \dots \quad (2)$$

where $\eta_0 = \eta_{ij}^0$, $\eta_1 = \eta_{ij}^1$, $\eta_2 = \eta_{ij}^2$, etc., then η_0 is a function of the

shear rate and the parameters. The yield stress σ_y is a function of the shear rate, and the parameters η_0 , η_1 , η_2 , etc., are functions of the shear rate. At low rates, where non-Newtonian behavior is not observed, the viscosity is a function of the shear rate, and the yield stress is a function of the shear rate. At high rates, where non-Newtonian behavior is observed, the viscosity is a function of the shear rate, and the yield stress is a function of the shear rate. The parameters η_0 , η_1 , η_2 , etc., are functions of the shear rate, and the yield stress is a function of the shear rate.

The following is a list of the names of the persons who have been appointed to the various positions in the various departments of the Government of the State of New York, for the year 1900.

[illegible]

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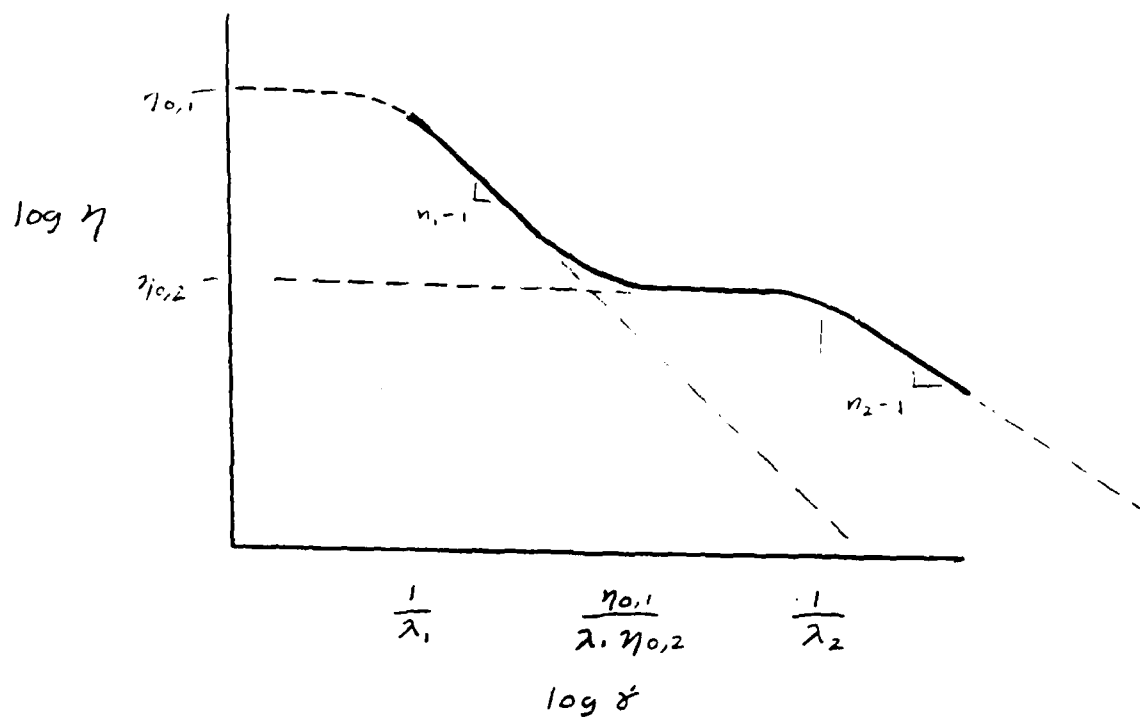


Figure 1. Typical steady shear viscosity curve for a filled polymer melts (solid curve). Dashed lines show the contribution of each term in Eqn. (2).

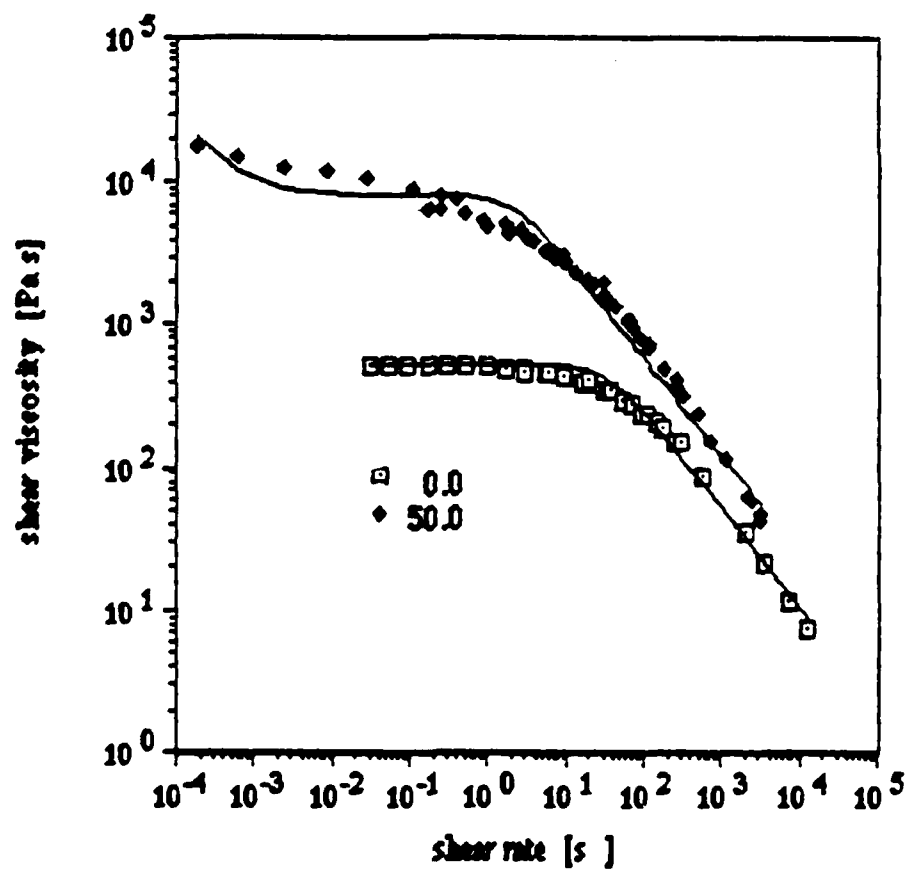
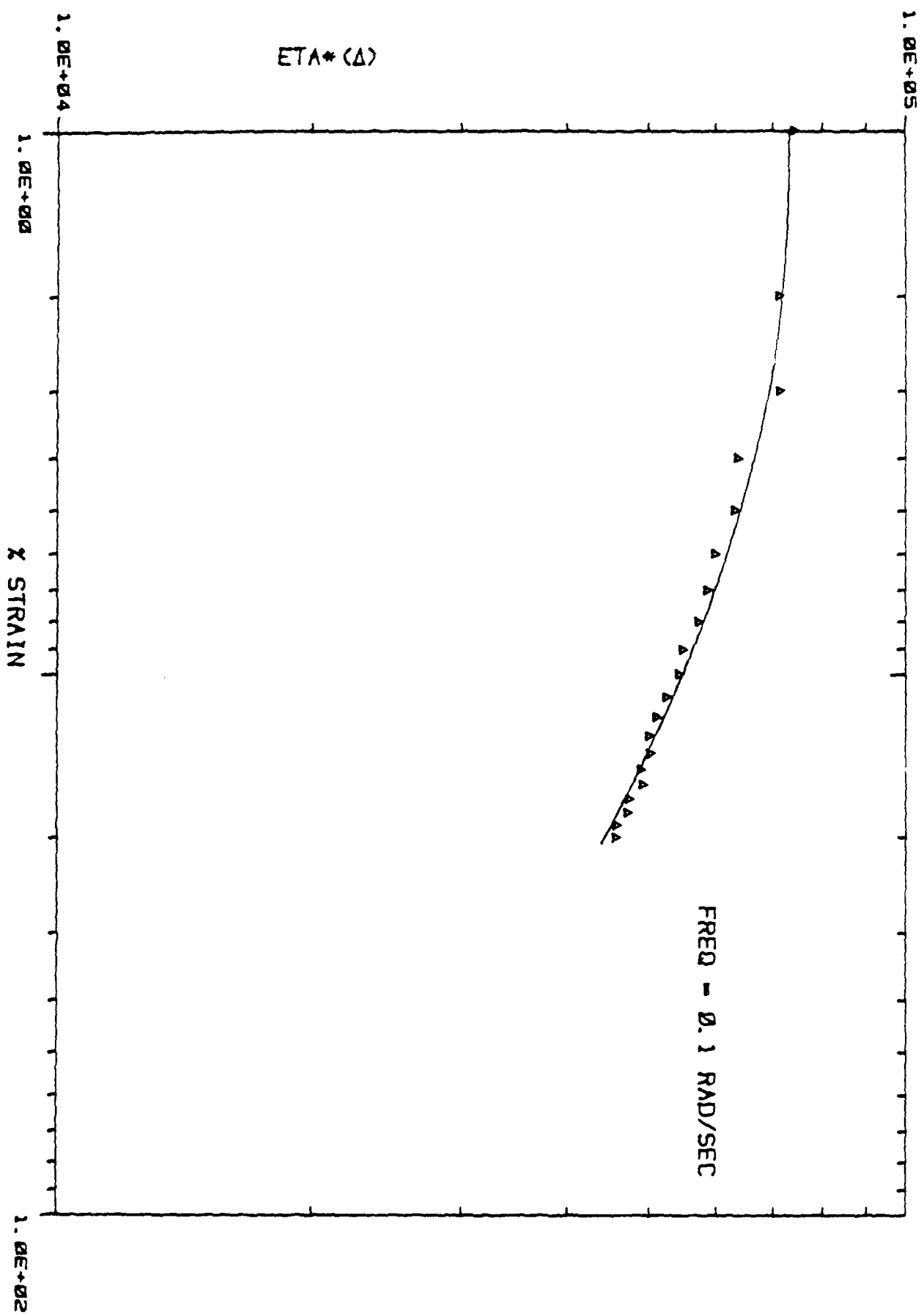


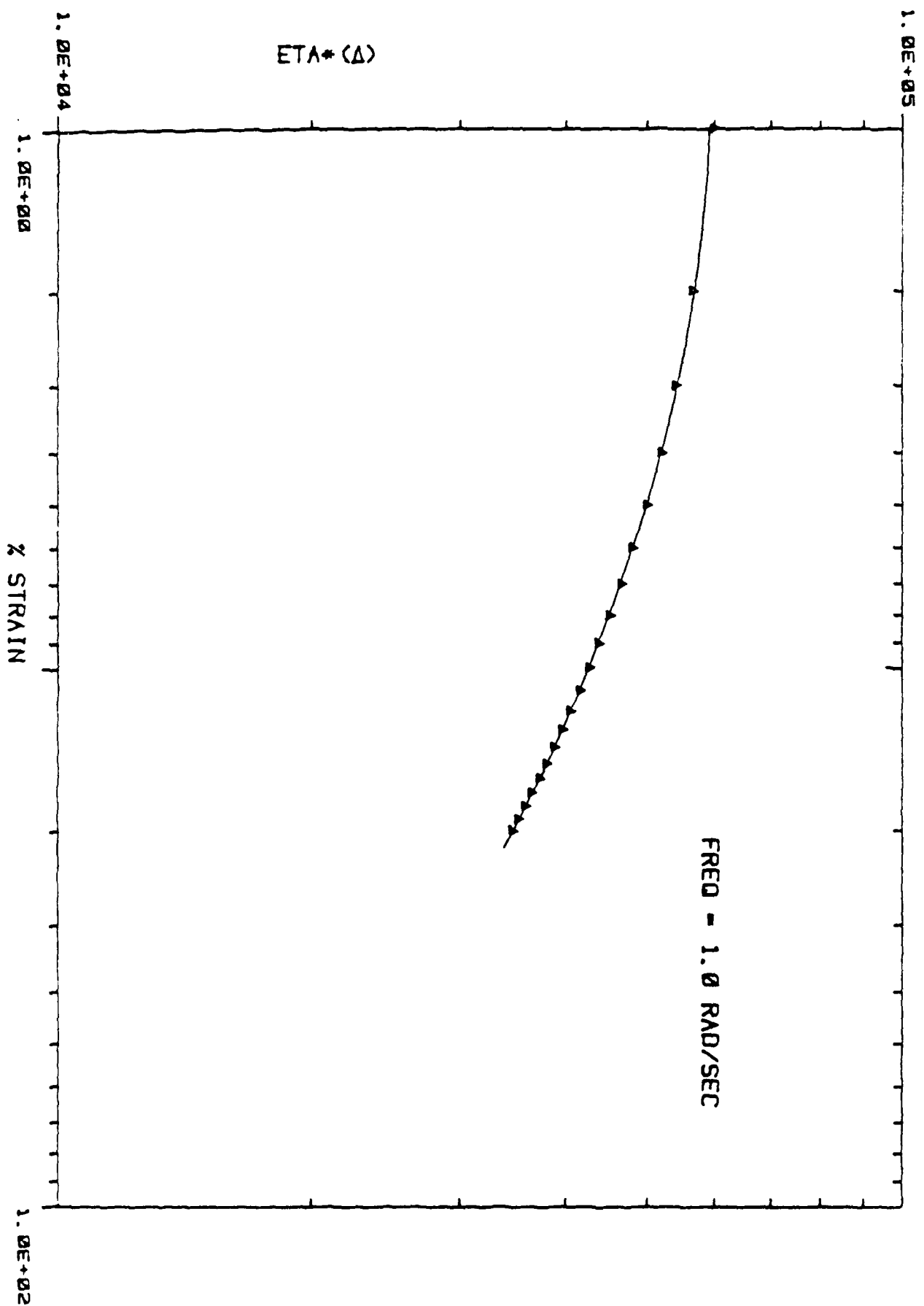
Fig 2

VISCASIL 600000/GLASS BEADS

TEMP - 30 C

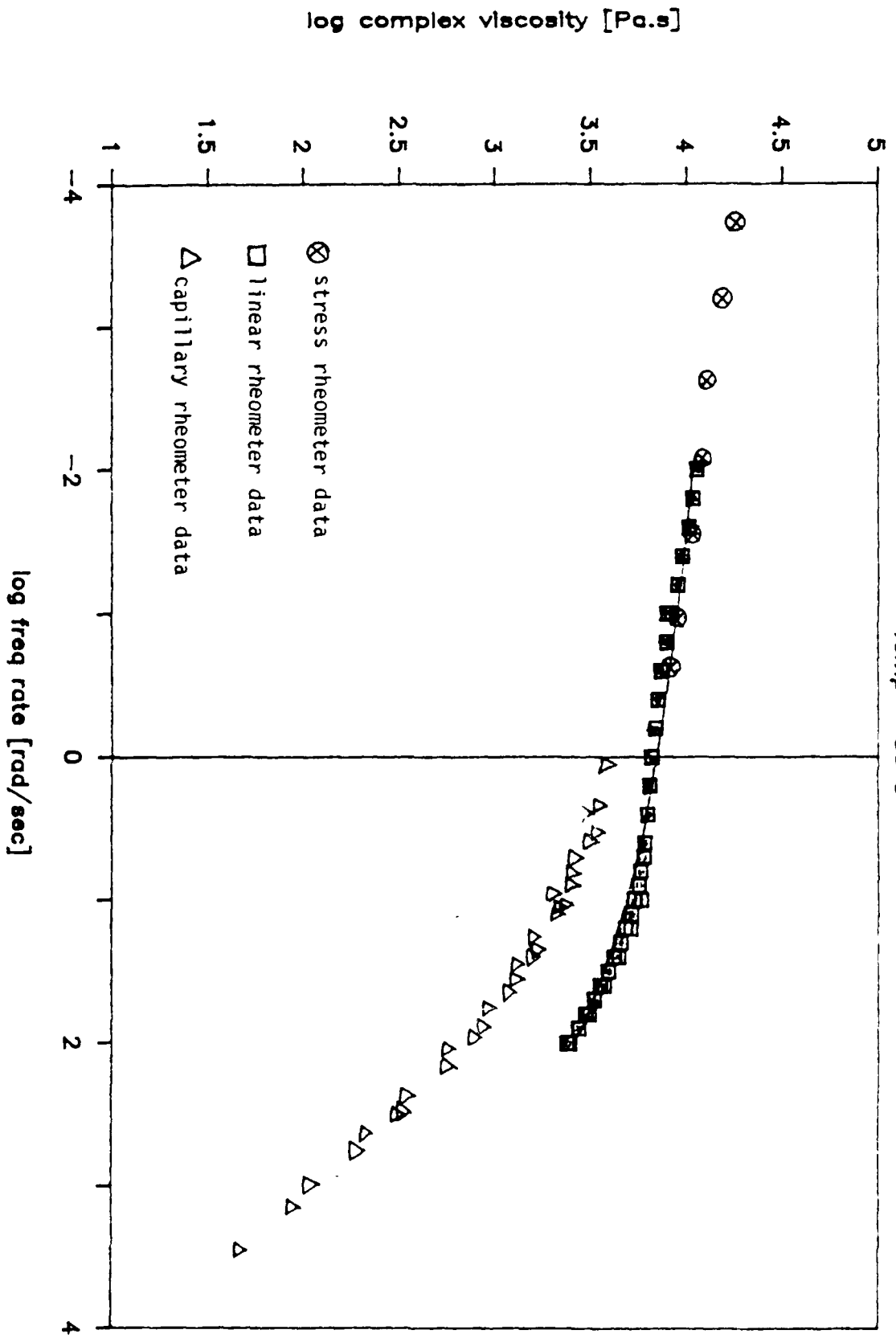


TEMP = 30 C



Viscasil 600000/glass beads

Temp = 30 C



Viscasil 600000/glass beads

Temp = 40°C

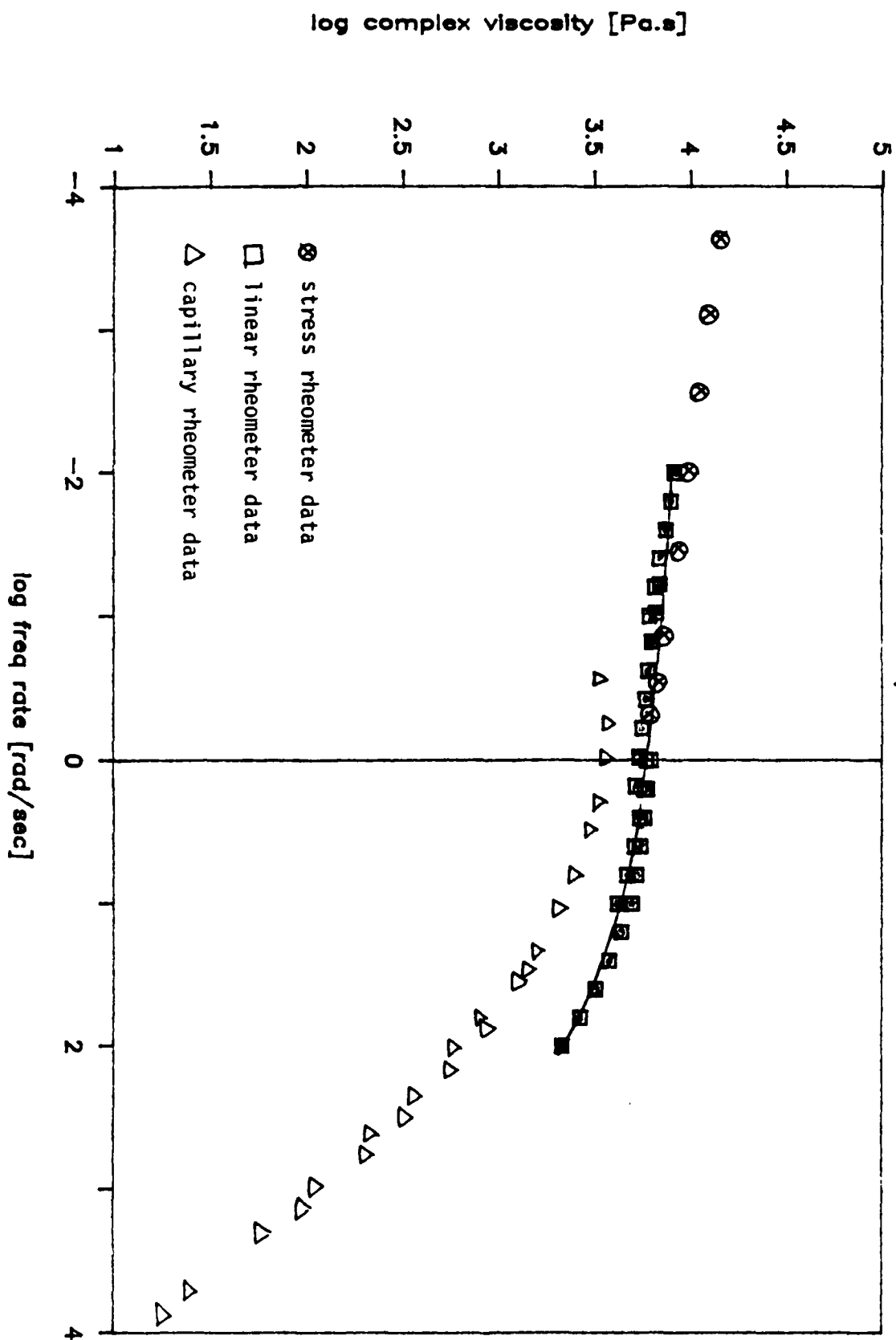
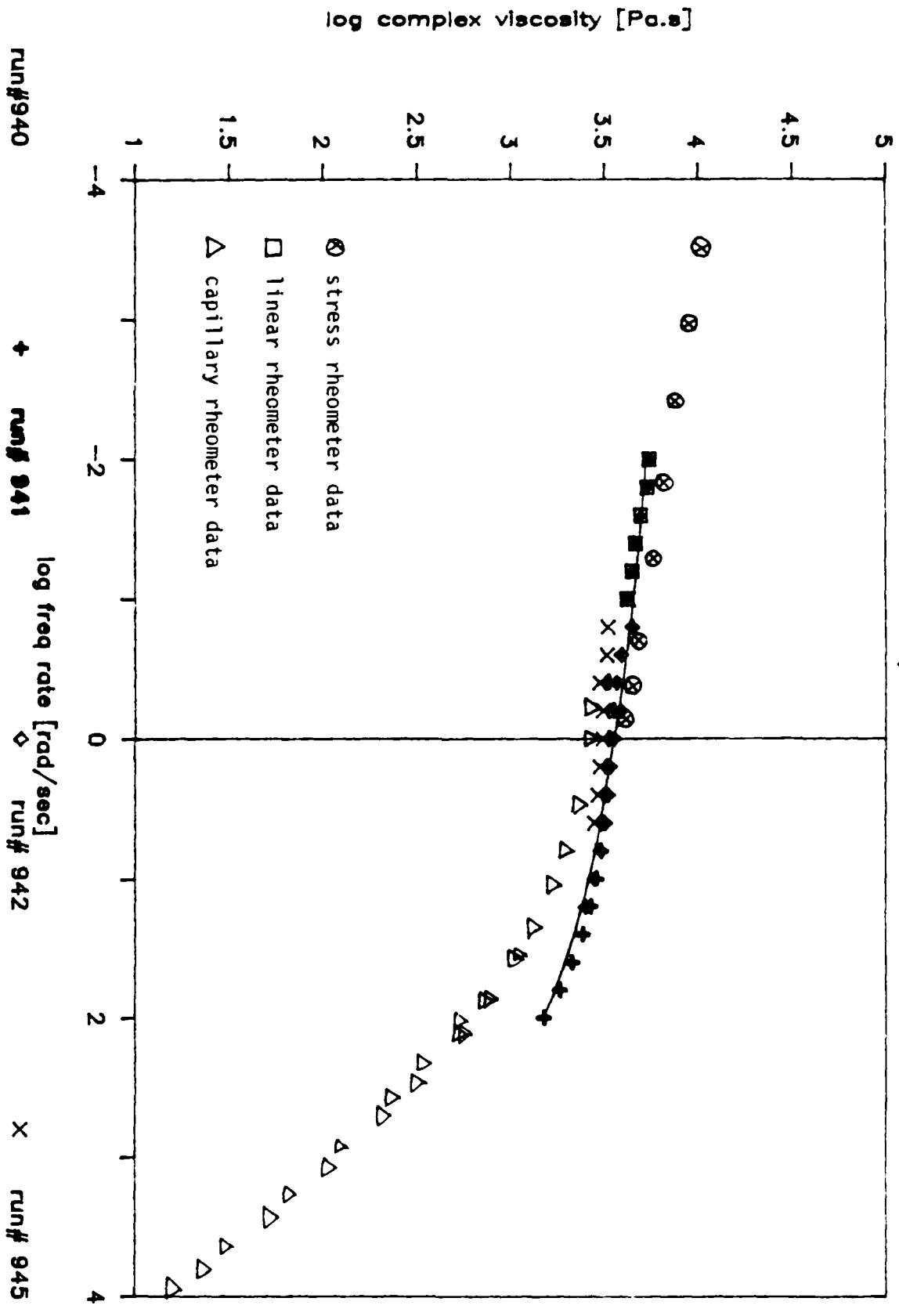


Fig 7

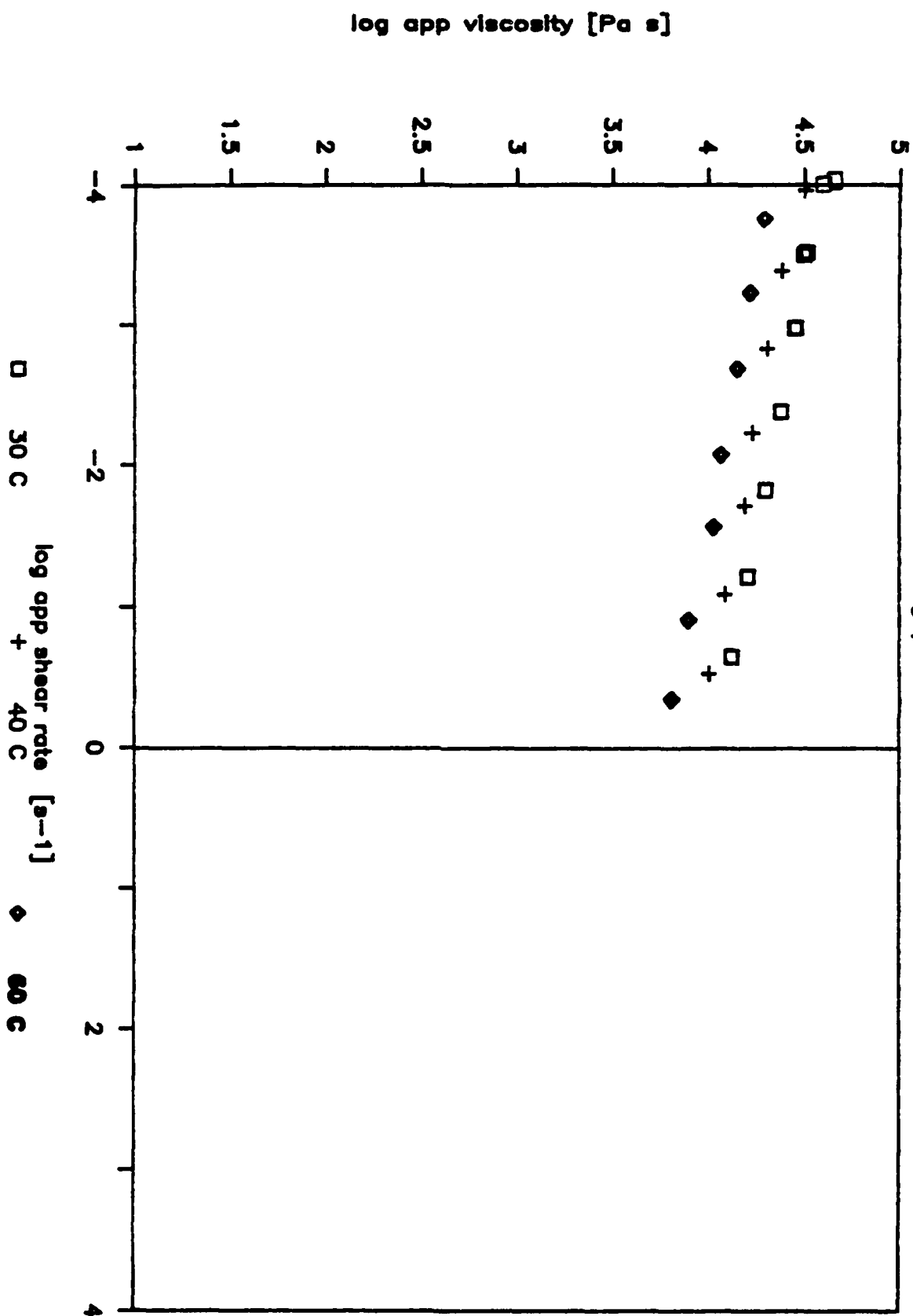
Viscasil 600000/glass beads

Temp = 60 C

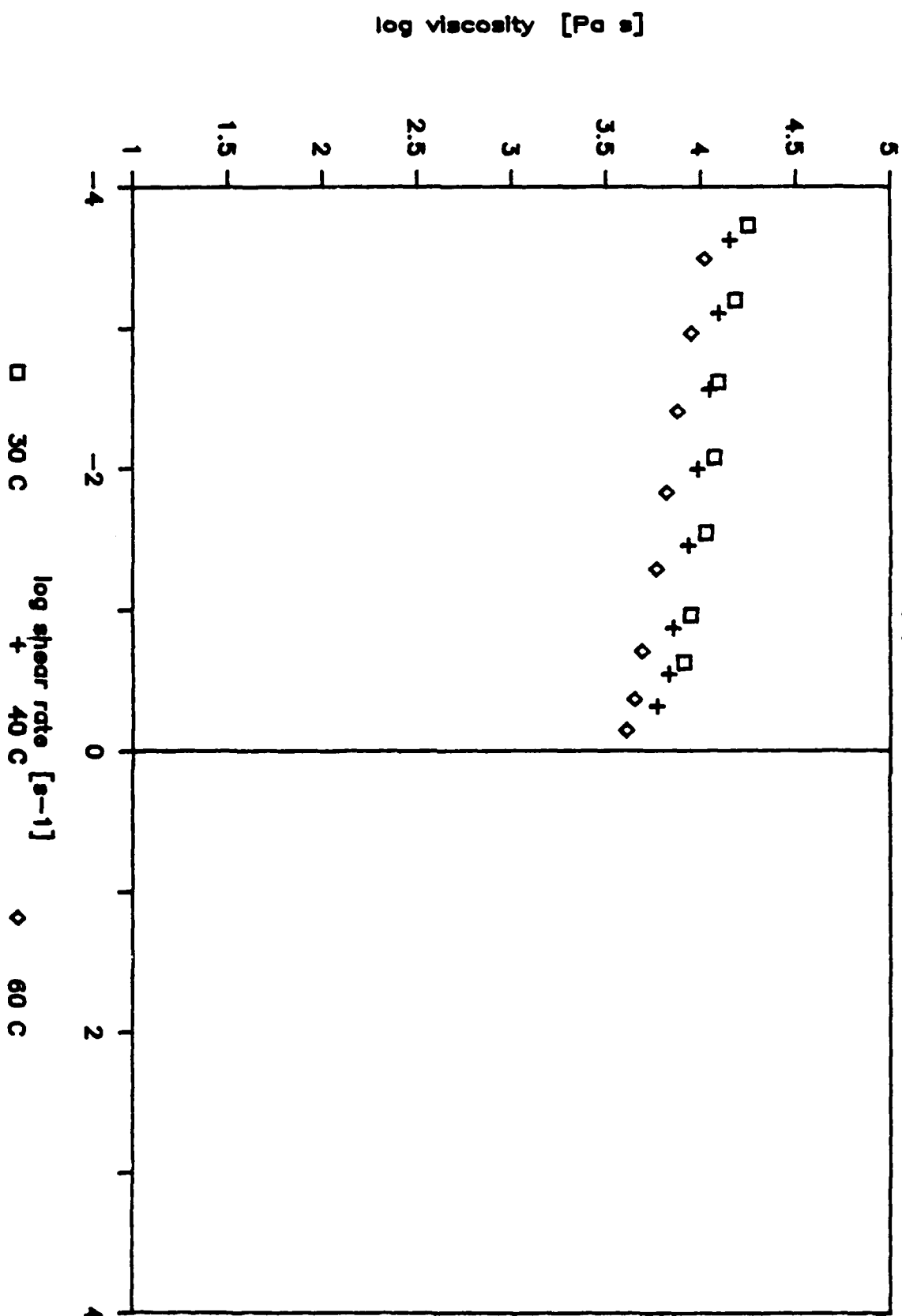


Viscasil/glass beads 55 vol%

gap = 2.000mm



Viscasil/glass beads 50 vol %
gap = 2.000mm



B. Rheology of Triblock Copolymers

Our program to investigate the effects of flow on the properties of triblock copolymers consists of two parts - evaluation of the rheological impact, and determination of the induced morphological changes. The results of the rheological study have been reported earlier, and work has begun on the second phase. In determining the effect of flow on the morphology of these materials, it will also be possible to understand more clearly the flow mechanism involved.

Two principle methods have been used to determine the morphology of a particular styrene-butadiene-styrene triblock copolymer: transmission electron microscopy (TEM), and small-angle x-ray scattering (SAXS). This report will concentrate on the SAXS results.

SAXS data was taken at the National Bureau of Standards in Gaithersburg, MD in order to use their 10m SAXS camera and software. Also the two-dimensional camera available there allows the detection of the entire scattering area, not just sections. This is very useful for measuring the scattering patterns of oriented materials as they will be anisotropic.

The results from the initial study show that as the shear strain is increased on the sample, the primary scattering peak due to the fundamental spacing of the cylinders on a hexagonal lattice becomes stronger. This is due to a more perfect alignment of the cylinders in the flow direction as strain increases. Preliminary quantitative analysis shows that the lattice parameter has a value of 278 Å which with an overall polystyrene volume fraction of .26 corresponds to cylinders of diameter 150 Å. A form factor peak occurring at higher angles is also consistent with a diameter of this magnitude (149 Å). The initial results from TEM show a slightly smaller diameter (133 Å).

V. Prediction of the Mechanical Behavior of Particulate Composites

Introduction

The energy balance type of approach to modelling the debonding behavior of highly filled composites such as propellants described in earlier reports is being more fully developed. This approach equates the change in strain energy of a sample during debonding to the work necessary to create new surfaces on the debonded particles. The predictions appear to be fairly accurate for isotropic composites with spherical filler particles. The experimental phase of the project is progressing. All of the apparatus for the experiments is now functional, and the preparation of samples is commencing. Comparisons of experimental results to model predictions will be forthcoming.

Experimental

A high-pressure gas dilatometer has been constructed and was recently tested for the first time. This instrument concurrently measures stress and volume changes which occur in a sample during uniaxial extension. Superimposed hydrostatic pressures of up to 1000 psi may be used. It

appears to operate properly, and is sensitive to small changes in pressure and load. Atmospheric testing of samples is scheduled to begin immediately. Some problems have been encountered in altering the existing software to work on the lab's new Zenith computer system, but are expected to be solved soon. The instrument is fully operational with the IBM AT software and the data collection will begin with that system.

Preparation of samples is proceeding very successfully. The bulk synthesis of polyurethane from tolylene 2,4-diisocyanate and diols or triols of poly (propylene oxide) to form void-free samples was accomplished after some trouble. Side reactions with water produce carbon dioxide bubbles throughout the samples. The entire reaction must be carried out under vacuum and the cast samples must be immediately transferred to a dessicator in order to produce void-free samples. The optimal isocyanate content for the reaction was determined. Composites of polyurethanes with up to 10 percent by volume glass beads have been made easily in small scale glassware. Larger batches of more highly filler systems have been attempted using the Baker-Perkins high-shear mixer purchased by Dr. Winter with LOVA funds, and appear to yield good results.

Theoretical

The models described in earlier meetings are being further developed. Current work is focusing on determining the proper void volume to add to the sample after debonding

in order to predict reasonable values of dilatation.

Progress is good, and the results will be presented at the September meeting of the Polymer and Materials Science and Engineering division of the American Chemical Society. A paper describing the derivations and the model predictions will soon be submitted for journal publication.

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